Explosive Properties of Polynitroaromatics

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FOREWORD (U)

A large number of polynitroaromatic compounds have been prepared at the Naval Weapons Center in programs directed toward the synthesis of new dense, powerful, and insensitive energetic materials. This report collates their explosive properties, including density, detonation velocity and pressure, and impact sensitivity, and attempts to identify structure/property correlations. Such correlations will provide greater understanding of energetic materials in general and should allow the rational, scientific identification of desirable target materials for new synthetic programs.

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(U)   A large number of polynitroaromatic compounds have been prepared in these laboratories over the last decade or so during programs to develop new energetic materials. This report documents their explosive properties, including density, detonation velocity and pressure, and impact sensitivity, and attempts to rationalize trends in those properties in terms of structure/property correlations.

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INTRODUCTION

A concentrated effort over the past decade or so has been devoted to the synthesis of new energetic materials in these laboratories. The aims of this synthetic effort have been the development of denser, more powerful explosive and propellant ingredients and the identification of less sensitive and, therefore, safer materials without sacrifice of current standards of performance. This synthetic program has been focussed largely on new cyclic (Reference 1) and more recently caged nitramines (Reference 2) (which will not be considered here), and on highly substituted polynitroaromatic compounds (Reference 3). Undoubtedly, the highlight of this latter work was the successful synthesis of hexanitrobenzene (HNB). The stratagem employed, namely nitration of a suitably substituted nitroaniline followed by the novel oxidation of the amine functionality using peroxydisulfuric acid, has proven useful in the synthesis of a whole range of polynitroaromatics. Another class of compounds, the nitrated and aminated benzofuroxans, has provided an equally fertile source of new energetic and insensitive ingredients (Reference 4).

The syntheses of these polynitroaromatic energetic materials and related benzofuroxans have been reported in a number of documents, including both Naval Weapons Center (NWC) technical reports and scientific journals. Therefore, these procedures will not be reproduced here. On the other hand, the explosive properties measured and/or calculated for these compounds, such as density, velocity and pressure of detonation, and particularly impact sensitivity, have been largely unreported. This report documents these properties for the series of such polynitro-aromatics and benzofuroxans prepared at NWC and attempts to rationalize them and identify underlying structure/property correlations. An understanding of such structure/property relationships is essential for the systematic, scientific formulation of appropriate targets for synthesis as potential new energetic materials.

RESULTS AND DISCUSSION

The compounds considered in this report are listed in Table 1, together with their entry numbers, acronyms, and chemical formulae. The structural formulae are given in the Appendix.

TABLE 1. Polynitroaromatic Compounds Studied.

No.	Acronym	Chemical name	Formula
1	HNB	Hexanitrobenzene	$C_6N_6O_{12}$
2	PNB	Pentanitrobenzene	$C_6HN_5O_{10}$
3	TetNB	1,2,3,5-Tetranitrobenzene	$C_6H_2N_4O_8$
4	TNB	1,3,5-Trinitrobenzene	$C_6H_3N_3O_6$
5	Picric acid	2,4,6-Trinitrophenol	$C_6H_3N_3O_7$
6	PNA	Pentanitroaniline	$C_6H_2N_6O_{10}$
7	TetNA	2,3,4,6-Tetranitroaniline	$C_6H_3N_5O_8$
8	TNA	2,4,6-Trinitroaniline	$C_6H_4N_4O_6$
9	DATB	1,3-Diamino-2,4,6-trinitrobenzene	$C_6H_5N_5O_6$
10	TATB	1,3,5-Triamino-2,4,6-trinitrobenzene	$C_6H_6N_6O_6$
11	HNBP	2,2',4,4',6,6'-Hexanitrobiphenyl	$C_{12}H_4N_6O_{12}$
12	DIPAM	3,3'-Diamino-2,2',4,4',6,6'-hexanitrobiphenyl	$C_{12}H_6N_8O_{12}$
13	CL-12	4,4'-Diamino-2,2',3,3',5,5',6,6'-octanitrobiphenyl	$C_{12}H_4N_{10}O_{16}$
14	DNBP	2,2',3,3',4,4',5,5',6,6'-Decanitrobiphenyl	$C_{12}N_{10}O_{20}$
15	DNBF	4,6-Dinitrobenzofuroxan	$C_6H_2N_4O_6$
16	ADNBF	7-Amino-4,6-dinitrobenzofuroxan	$C_6H_3N_5O_6$
17	CL-14	5,7-Diamino-4,6-dinitrobenzofuroxan	$C_6H_4N_6O_6$
18	CL-17	7-Amino-4,5,6-trinitrobenzofuroxan	$C_6H_2N_6O_8$
19	CL-18	8-Amino-7-nitrobenzobisfuroxan	$C_6H_2N_6O_6$
20	BTF	Benzotrifuroxan	$C_6N_6O_6$
21	PNT	Pentanitrotoluene	$C_7H_3N_5O_{10}$
22	2,3,4,5-TetNT	2,3,4,5-Tetranitrotoluene	$C_7H_4N_4O_8$
23	2,3,4,6-TetNT	2,3,4,6-Tetranitrotoluene	$C_7H_4N_4O_8$
24	2,3,5,6-TetNT	2,3,5,6-Tetranitrotoluene	$C_7H_4N_4O_8$
25	2,4,6-TNT	2,4,6-Trinitrotoluene	$C_7H_5N_3O_6$
26	2,3,4-TNT	2,3,4-Trinitrotoluene	$C_7H_5N_3O_6$
27	3,4,5-TNT	3,4,5-Trinitrotoluene	$C_7H_5N_3O_6$
28	TetN-o-Tol	2-Amino-3,4,5,6-tetranitrotoluene	$C_7H_5N_5O_8$
29	TetN-m-Tol	3-Amino-2,4,5,6-tetranitrotoluene	$C_7H_5N_5O_8$
30	TetN-p-Tol	4-Amino-2,3,5,6-tetranitrotoluene	$C_7H_5N_5O_8$
31	HNDPM	2,2',4,4',6,6'-Hexanitrodiphenylmethane	$C_{13}H_6N_6O_{12}$
32	Picryl azide	2-Azido-1,3,5-trinitrobenzene	$C_6H_2N_6O_6$
33	CL-16	Azidopentanitrobenzene	$C_6N_8O_{10}$
34	DDNP	2-Diazo-4,6-dinitrophenol	$C_6H_2N_4O_5$
35	5-Cl-DDNP	5-Chloro-2-diazo-4,6-dinitrophenol	$C_6HN_4O_5Cl$
36	Me NO₂-DDNP	3-Methyl-2-diazo-4,5,6-trinitrophenol	$C_7H_3N_5O_6$
37	Tetryl	N-Methyl-N,2,4,6-tetranitroaniline	$C_7H_5N_5O_8$
38	(MeNO₂N)-22	N-Methyl-2-amino-N,3,4,5,6-pentanitrotoluene	$C_8H_6N_6O_{10}$
39	(MeNO₂N)-23	N-Methyl-3-amino-N,2,4,5,6-pentanitrotoluene	$C_8H_6N_6O_{10}$

Table 2 lists the various explosive properties determined for these polynitro-aromatics, including predicted velocity of detonation and detonation pressure, calculated and measured densities, oxygen balance, and impact sensitivity.

TABLE 2. Explosive Properties of Polynitroaromatic Compounds.

No.	Acronym	V of D, m/s	P_{CJ}, kbar	ρ_{calc}, g/cm^3	ρ_{obs}, g/cm^3	OB_{100}	$h_{50\%}$, cm	log h
1	HNB	9100	393	1.97	1.99	3.45	11	1.04
2	PNB	8700	355	1.91	. . .	2.97	11	1.04
3	TetNB	8130	302	1.83	1.82	1.55	28	1.45
4	TNB	7280	223	1.73	1.68	-1.41	71	1.85
5	Picric Acid	7360	231	1.77	1.77	-0.48	64	1.81
6	PNA	8810	366	1.92	1.86	1.89	22	1.35
7	TetNA	8280	317	1.84	1.87	0.37	47	1.67
8	TNA	7500	244	1.75	1.76	-1.75	141	2.15
9	DATB	7690	262	1.77	1.84	-2.06	>200	>2.30
1 0	TATB	7860	278	1.78	1.94	-2.33	>200	>2.30
1 1	HNBP	7320	226	1.78	1.69	-0.92	70	1.84
1 2	DIPAM	7570	250	1.80	1.79	-1.32	67	1.83
1 3	CL-12	8280	317	1.89	1.82	0.74	20-95[a]	. . .
1 4	DNBP	8660	352	1.95	1.86	2.65	. . .	. . .
1 5	DNBF	7700	263	1.86	1.76	-0.88	76	1.88
1 6	ADNBF	7890	280	1.88	1.90	-1.25	100	2.00
1 7	CL-14	8050	295	1.89	1.95	-1.56	120	2.08
1 8	CL-17	8560	342	1.96	1.94	0.70	56	1.75
1 9	CL-18	8230	312	1.98	1.93	-0.79	56	1.75
2 0	BTF	8420	330	2.12	1.90	0.00	53	1.72
2 1	PNT	8230	312	1.82	1.76	0.95	18	1.25
2 2	2,3,4,5-TetNT	7600	253	1.73	1.71	-0.74	15	1.16
2 3	2,3,4,6-TetNT	7600	253	1.73	1.71	-0.74	19	1.27
2 4	2,3,5,6-TetNT	7600	253	1.73	1.69	-0.74	25	1.39
2 5	2,4,6-TNT	6670	166	1.63	1.67	-3.08	98	1.99
2 6	2,3,4-TNT	6670	166	1.63	. . .	-3.08	56	1.75
2 7	3,4,5-TNT	6670	166	1.63	. . .	-3.08	107	2.03
2 8	TetN-o-Tol	7770	269	1.75	1.72	-1.05	36	1.55
2 9	TetN-m-Tol	7770	269	1.75	1.73	-1.05	37	1.57
3 0	TetN-p-Tol	7770	269	1.75	1.72	-1.05	47	1.67
3 1	HNDPM	7030	200	1.72	1.71	-1.80	39	1.59
3 2	Picryl Azide	8230	312	1.74	. . .	-0.79	19	1.28
3 3	CL-16	9220	404	1.89	. . .	2.33	17	1.23
3 4	DDNP	7220	217	1.71	1.72	-1.84	9	0.97
3 5	5-Cl-DDNP	. . .	. . .	. . .	1.88	-0.82	8	0.90
3 6	Me-NO$_2$-DDNP	7550	248	1.72	. . .	-1.12	8	0.89
3 7	Tetryl	7770	269	1.73	1.73	-1.04	25	1.40
3 8	(MeNO$_2$N)-22	7950	286	1.74	1.72	-0.58	21	1.34
3 9	(MeNO$_2$N)-23	7950	286	1.74	1.71	-0.58	18	1.26

[a] CL-12 shows a marked dependence of impact sensitivity on particle size.

VELOCITIES OF DETONATION

A number of methods are available for the calculation of the detonation parameters of an explosive. At least in theory, the velocity of detonation may be determined completely by the thermohydrodynamics of the explosive, with the independent variables being chemical composition and density. All other variables should be calculable using the thermohydrodynamic theory and an appropriate equation of state. Computer programs available for these computations include TIGER (Reference 5), HEMP (Reference 6), and STRETCH BKW (Reference 7). However, each is moderately complex, requires a knowledge of the equation of state of the explosive (which in turn requires extensive experimental measurement of the detonation phenomena) but still retains a considerable empirical character. Clearly, these methods are inappropriate for the estimation or prediction of properties for a compound yet to be prepared.

Several attempts have been made to relate detonation parameters with more accessible properties of an explosive. The most successful of these attempts appears to be that of Kamlet, who showed that a fairly simple relationship exists between detonation velocity and the heats of formation of the explosive and its detonation products, the explosive density, and the quantity of gaseous detonation products (Reference 8). Again, the requirement for a knowledge of the density and heat of formation of the explosive limits the value of this method as a predictive tool for a proposed new compound.

The method most commonly used to predict the detonation parameters of a prospective new explosive is that of Rothstein and Petersen (Reference 9), and is based *on an observed linear relationship, for some 64 explosives,* between the velocity of detonation at theoretical maximum density (D') and a factor (F),

$$D' = (F - 0.26)/0.55.$$

The factor (F) was derived solely from molecular formulae and structures and required no prior knowledge of any properties other than to know or to guess whether the explosive was a solid or a liquid, making the method ideal for predicting the properties of an as-yet unprepared compound. The factor is expressed as

$$F = (100/MW) \cdot (n_O + n_N - n_H/2n_O + A/3 - n_B/1.75 - n_C/2.5 - n_D/4 - n_E/5) - G,$$

where MW = molecular weight,
         n_O = number of oxygen atoms,
         n_N = number of nitrogen atoms,
         n_H = number of hydrogen atoms,
         n_B = number of oxygen atoms in excess of H_2O, CO_2 oxygen balance,
         n_C = number of oxygen atoms doubly bonded to carbon,
         n_D = number of oxygen atoms singly bonded to carbon.
         n_E = number of nitrato groups,
         G = 0.4 for liquids, 0 for solids, and
         A = 1 for aromatics, 0 for nonaromatics.

While such a simple empirical relationship has obvious advantages, it nonetheless has limitations. Principal among these is its inability to distinguish between either positional or structural isomers, or between polymorphs.

There is little that needs to be said about the calculated velocities of detonation for the polynitroaromatics discussed here, except that they cover a range of about 6700 m/s for the isomeric TNTs to over 9000 m/s for HNB and CL-16. This corresponds to a range of 166 to 403 kbar for detonation pressures, which may be a more relevant parameter for many applications. There were no unexpected results from these empirical calculations. Note, however, that velocity of detonation is a function of density, although that parameter is not a direct, explicit input into the empirical formula used here. Conceivably, the velocities of detonation should be adjusted for those compounds whose densities deviate significantly from the values predicted.

DENSITIES

Density is one of the easiest parameters to be calculated for a proposed target energetic material, or to be measured for a newly synthesized compound. The density of an energetic material is of paramount importance, on the one hand to load the greatest quantity into a given volume or to minimize the space required for a given weight of explosive charge, and on the other hand because the performance of an explosive, the energy released, is directly related to its density. Thus, velocity of detonation is a linear function of density, while detonation pressure is proportional to density squared. Further, if in a given formulation, an energetic ingredient could be replaced by one with similar energy and sensitivity but increased density, the same performance could be obtained with a lower loading of energetic solids and a higher loading of binder/desensitizer, and a decrease in the sensitivity of the formulation could be expected.

A method has recently been developed for the calculation of crystal densities from crystal packing arrangements (Reference 10). However, this method is quite complex, requiring determination of the molecular structure and probable conformation, determination of trial crystal structure models, and finally minimization of energy of these models with respect to unit cell parameters and calculation of density from the resultant unit cell volume, and substantial quantities of computing time are necessary. Consequently, one of a range of "group additivity" methods is commonly used. The one employed in this study is that of Holden (Reference 11). This method is based on the assumption that the average or "normal" density of an organic compound may be calculated by dividing its molecular weight by its molecular volume, and that the molecular volume may be calculated by summation of its component atomic or group volumes and correction for group effects such as aromatic and nonaromatic rings and hydrogen bonding. The particular feature of the Holden method is that the atomic and group volumes and corrections were derived from a set of 5£5 energetic compounds and their precursors, and should, therefore, be optimized for prediction of similar new explosives and propellants. On the other hand, the method should not be expected to handle well radically new molecular structures or functional groupings. In addition, this method also lacks the subtlety to distinguish between positional and structural isomers or polymorphs.

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The polynitroaromatics considered in this report have experimentally determined densities (gas pycnometry or X-ray crystallography) ranging from about 1.65 g/cm^3 for TNT to nearly 2.00 g/cm^3 for HNB. In each case, the density predicted by the Holden group additivity method is in reasonable agreement with the experimental value, as shown in Figure 1, with the greatest deviation being about 6%. This method consistently overestimates densities for compounds containing the methyl group, the furoxan moiety, or biphenyl skeletal ring systems (which can be expected to adopt an orthogonal configuration with a less efficient crystal packing pattern). On the other hand, molecules which contain alternating nitro and amino groups, such as DATB, TATB, and CL-14, show unexpectedly higher experimental densities believed to be due to electron delocalization and to intra- and intermolecular hydrogen bonding between these groups. (It should be noted that the presence of alternating nitro and amino groups around the aromatic ring compensates for the furoxan moiety in both ADNBF and CL-14. A similar effect is noticed in the cases of tetraaminohexanitrobiphenyl ("bis-TATB"), which matches the predicted density, and diaminotrinitrotoluene, which exceeds it; again the presence of alternating nitro and amino groups compensates for the density-lowering effects of the orthogonal biphenyl skeleton and the methyl group, respectively.) These materials with higher densities than anticipated, "outriders," form a group of interesting explosives which should also exhibit detonation parameters in excess of those predicted on the basis of empirical calculations.
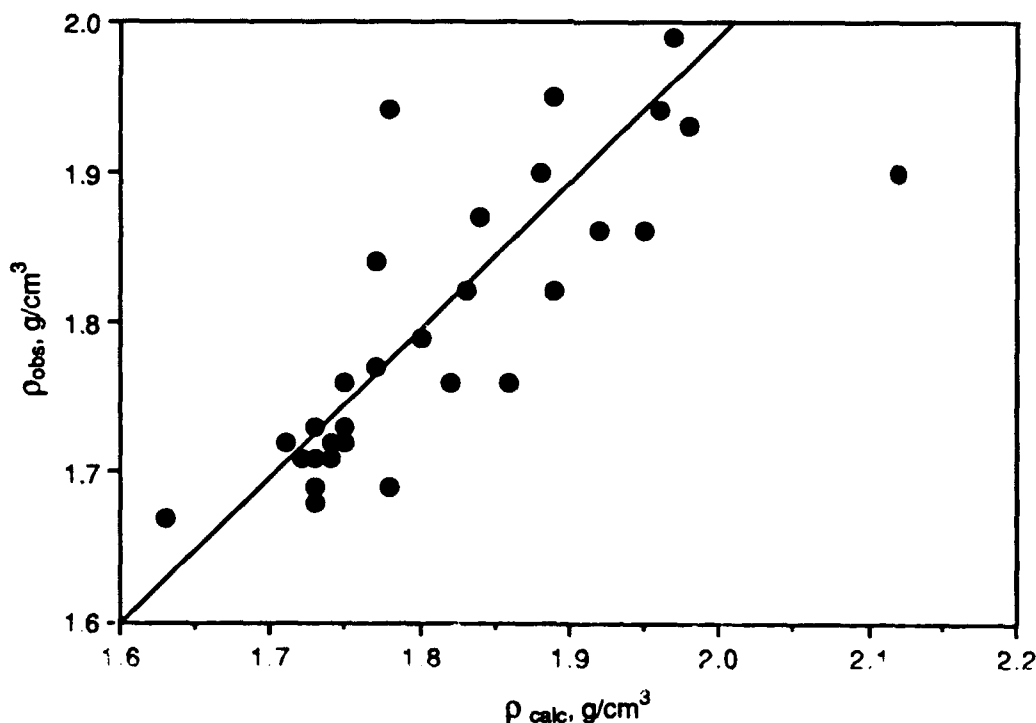
FIGURE 1. Correlation of Calculated and Observed Densities.

IMPACT SENSITIVITIES

While satisfactory (or at least adequate) models are available to estimate the density and performance (detonation velocity and pressure) of a potential new energetic material, our understanding of explosive structure/sensitivity relationships is not as well developed. Superficially, one of the simplest tests available for screening new explosives for sensitivity to accidental and environmental stimuli and for identifying potential roles in which they might be usefully employed is the drop weight impact test, and this is consequently one of the first tests carried out. In our laboratory impact sensitivity is determined using the Bureau of Mines (B of M, Pittsburgh, Penna.) impact machine with the Type 12 tool and 2.5 kg drop weight. The explosive (35 mg) is placed in a roughly conical pile on a 1-inch square of garnet paper and placed on the polished, flat tool steel anvil. The polished, flat surface of the tool steel striker is placed on top of the sample and a 2.5 kg weight is dropped from a predetermined height onto the striker. The result of the event, explosion or otherwise, is determined by a combination of sound, smell, and visual inspection of the sample and paper. The drop height is varied according to the Bruceton "staircase" method, the height being decreased if the previous event was an explosion or increased if it was not. Drop heights are equally spaced in the logarithm of the height at 0.1 log unit intervals. (The log of a 10-cm drop is taken as 1.0.) A sequence of 25 tests is carried out, and the result is quoted as $h_{50\%}$, the height at which 50% of tests result in explosions.

However, although the drop weight impact test is easy to carry out and although it has proven useful as a crude screening procedure to classify explosives as sensitive, moderately sensitive, or insensitive, it has proven frustratingly inaccurate and seemingly irreproducible. Thus, a material can give different results on two apparently identical machines, or even on the same machine on different days. Some probable causes of variation include the base on which the apparatus stands, minor differences in the guide rails and friction on the falling weight, confinement of the sample, humidity, and operator differences in determination of explosion or otherwise. Considerable effort has been expended in an attempt to instrument the test, measuring *inter alia* noise production and gas evolution on explosion, endeavoring to eliminate potential operator variables, but with only limited success. Indeed drop weight impact sensitivities for twice recrystallized TNT have varied from below 100 cm to above 250 cm. It is small wonder that Bowden declared (Reference 12) that hitting a material with a hammer is a pastime more befitting a carpenter than a scientist! However, all impact testing reported here was carried out using the same machine under the same conditions, and largely by the same skilled operator. Further it was hoped that, while too much should not be made of the precise impact sensitivity of an individual compound, if a sufficiently large number of structurally related compounds are tested, these individual oddities and vagaries might tend to offset each other, and meaningful trends might evolve.

Since the criterion for an explosion depends on a critical propagation of reaction, the drop weight impact test does not yield an unequivocal and unencumbered measure of the sensitivity of an explosive. (Indeed in the Rotter impact test, in which the criterion for explosion is the evolution of gas, the volume of gas evolved is interpreted as an indication of the ease of propagation of the explosive reaction.) The conclusion was reached long ago that the impact initiation of explosives involves the creation of hot spots, which must reach a localized temperature of about 500°C if propagation of the

explosive reaction is to be sustained (Reference 13). Factors which might contribute to the critical generation of hot spots include

kinetics of decomposition,
heat evolved in decomposition,
heat capacity,
thermal conductivity.
latent heats of fusion and evaporation,
crystal hardness,
crystal shape,
crystal cracks and defects, and
trapped gases, etc.

By restricting the study to organic solids and by resting the explosive samples on garnet paper, it was hoped that the effects of crystal properties would be minimized, as would the variations in physical properties.

Several groups have published results of studies into relationships between the structure of energetic materials and their sensitivity to impact initiation. The first studies were by Kamlet and Adolph, who studied a large number of nitroaliphatics and nitramines (Reference 14) and nitroaromatics (Reference 15). They were able to identify a broad general trend in which the logarithm of 50% drop height (log $h_{50\%}$) decreased with increasing oxygen balance (OB_{100}). If the explosives were restricted to a single class of compounds, where a common decomposition pathway might be inferred, reasonably good linear correlations were found. Jain considered a variant of this approach and found good correlations of his "valence parameter" with impact sensitivity, velocity of detonation, and heat of explosion (Reference 16). Storm and Stine reconsidered the data of Kamlet and Adolph for polynitroaromatics and claimed that a very much improved correlation of log $h_{50\%}$ with OB_{100} (-0.97 to -1.00) could be obtained if the explosives were restricted to a series of very closely related compounds, and that these correlations could be used to predict very accurately the impact sensitivity of a new member of that series (Reference 17). These results look very impressive but, given the accepted reliability of log $h_{50\%}$ (±0.10), such outstanding correlations may be fortuitous and misleading. Mullay reported a correlation between impact sensitivities and molecular electronegativities of energetic materials (Reference 18). Nielsen (Reference 2) extended Stals' work (Reference 19) and proposed a correlation between impact sensitivity and the dissociation energy for the weakest bond, which could be calculated empirically if all bond lengths were known. However, the accuracy of these empirical calculations was limited, and bond lengths were not necessarily available. Delpuech and Cherville carried out quantum mechanical calculation of critical bond polarities and reported correlations within families of explosives (Reference 20).

We chose to consider the simple procedure of Kamlet and Adolph (References 14 and 15). These authors were able to identify a relationship between the impact sensitivity of a polynitroaromatic and its oxygen balance, OB_{100}, which can be related to the energy available in the explosive (Reference 15). Oxygen balance is calculated using the formula

$$OB_{100} = 100(2n_O - n_H - 2n_C - 2n_{COO})/MW$$

where n_O = number of oxygen atoms,

n_H = number of hydrogen atoms,

n_C = number of carbon atoms,

n_{COO} = number of carboxyl groups, and

MW = molecular weight.

Further, they were able to account for the increased sensitivity over simple polynitro-aromatics, in which the initiating step is presumably a scission of the $C-NO_2$ bond, of those compounds which contained a C-H bond alpha to the polynitroaromatic ring. In the latter group of compounds, the initiating step was identified as scission of the C-H bond. Support for this mechanism was derived from studies of the thermal decomposition of TNT, in which products formed by reaction at the methyl group were isolated and identified (Reference 21), and for which a primary kinetic isotope effect was observed when the methyl group was labelled with deuterium (Reference 22). Kamlet and Adolph coined the term "trigger linkage" for the site of the initiating step; Delpuech and Cherville designate it as the "privileged bond" (Reference 20). Kamlet and Adolph also concluded, not unreasonably, that if a compound contains structural features of more than one sensitivity category, then its impact behavior should conform more closely with the more sensitive one.

With only two exceptions, the nitroaromatics considered by Kamlet and Adolph in 1979 contained no more than three nitro groups on one ring (Reference 15). Since that time, many more highly nitrated compounds have become available, most of which are included in this study. Indeed, of the 40-odd compounds considered here, about half contain four or more nitro groups on the same ring. The relationship of the impact sensitivity of these compounds with their oxygen balance is illustrated in Figure 2. The first point to be noted, after the expected general tendency towards increased sensitivity with increased oxygen balance, is that direct comparisons should be restricted in the first place to structurally similar materials. Thus, the diazophenols and the aromatic azides are much more sensitive to impact than are the general body of polynitro-aromatics, and the dependence on oxygen balance is less pronounced. It is reasonable to infer that the "trigger linkages" in these compounds are associated with the diazonium and azido functionalities, and that they are influenced relatively little by the remainder of the molecule. A similar result is observed for polynitroaromatics containing the nitramine grouping. Once again these compounds are considerably more sensitive, and the initial reaction on impact is believed to be cleavage of the $N-NO_2$ bond.
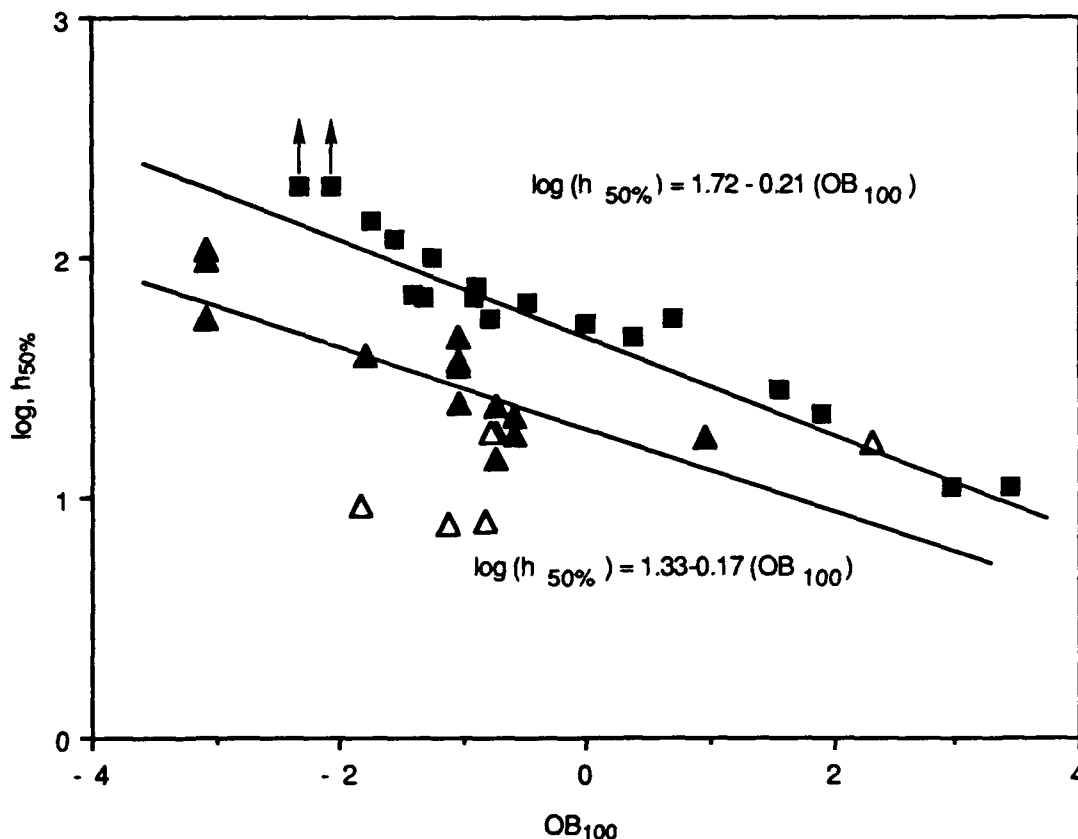
FIGURE 2. Correlation of Impact Sensitivity With Oxygen Balance.

Second, the results for those compounds which do not contain an α C-H bond may be fitted to a linear relationship

$$\log (h_{50\%}) = 1.72 - 0.21 \ (OB_{100})$$

with a correlation coefficient of 0.96 and a standard error of 0.10. These results are comparable with those of Kamlet and Adolph (Reference 15), although the constants are slightly different because the impact sensitivities were determined on a different drop-weight machine. We want to stress again that the standard error corresponds with the height increment on the drop-weight machine, the commonly accepted accuracy, and reproducibility of the test procedure. The benzofuroxans correlate well with the polynitroaromatics in this investigation, and the amine groups appear to show little desensitizing effect over that indicated by the reduction in oxygen balance.

The polynitroaromatic compounds containing an α C-H group are consistently more sensitive to impact than are similar compounds with the same oxygen balance but without the α C-H group, and they appear to form a separate class. These results can also be fitted to a linear relationship,

$$\log (h_{50\%}) = 1.33 - 0.17 \ (OB_{100}),$$

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but here the correlation coefficient is only 0.87 and the standard error is increased to 0.14. This increased spread of data was not unexpected since most of the results were for sets of positional isomers. However, since the impact sensitivities for each set of isomers were measured at the same time and by the same operator, we are able to use this spread of results to draw some interesting conclusions about the effects of positional isomerism.

The first compounds considered were the isomeric tetranitrotoluidines (28 through 30). The *ortho* and *meta* derivatives (28, 29) had impact sensitivities of 36 and 37 cm, respectively, while the *para* isomer (30) had an impact sensitivity of 47 cm. The obvious structural difference is that 28 and 29 each contain three contiguous nitro groups about the aromatic ring, whereas 30 lacks this feature. It is known that the central of three contiguous nitro groups is rendered more prone to chemical reaction by a combination of electronic and steric factors, and it has been suggested that this group may be more activated towards rearrangement to a nitrito functionality, where O—N bond cleavage should be facilitated (Reference 23).
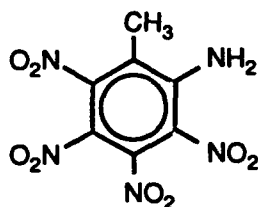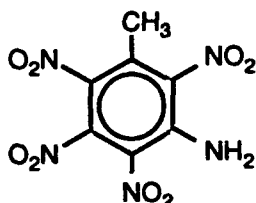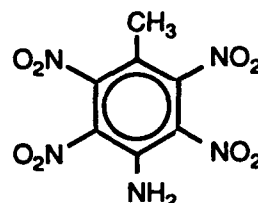
28	29	30
36 cm	37 cm	47 cm

The second group of compounds considered consisted of the isomeric tetranitrotoluenes (22-24). The 2,3,4,5-tetranitro isomer (22), with four contiguous nitro groups around the aromatic ring, had an impact sensitivity of 15 cm; the 2,3,4,6 isomer (23), with three contiguous nitro groups, had an impact sensitivity of 18 cm; the 2,3,5,6 isomer (24), with only two contiguous nitro groups, had an impact sensitivity of 25 cm. The differences in sensitivity are not large, but the variation shows the expected trend. Given that they were determined by the same operator on the same machine at the same time, we believe that these results support our hypothesis that, in a polynitroaromatic containing three contiguous nitro groups, the central nitro group is activated to reaction, probably nitro/nitrito rearrangement, and this functional group provides the "trigger linkage" for impact initiation. (Note that the tetranitrotoluenes (22-24) are more sensitive than the tetranitrotoluidines (28-30). Clearly, in this class of compounds, the amine functionality does act as a desensitizing group; apparently, this is not universally the case, as will be discussed below.)
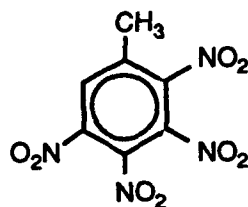
22

15 cm
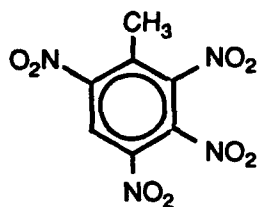
23

18 cm
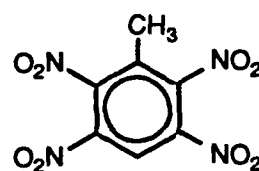
24

25 cm

However, the results of Kamlet and Adolph strongly indicate that the α C-H bond is involved in the initiating reaction (Reference 15); the results reported here certainly support that contention. In an attempt to clarify this question, three of the isomeric trinitrotoluenes were examined. 2,4,6-TNT (α, 25), with no adjacent nitro groups but with the methyl group having two nitro group neighbors, had an impact sensitivity of 100 cm. 2,3,4-TNT (β, 26), with three contiguous nitro groups and with the methyl group having one nitro group neighbor, had an impact sensitivity of 56 cm. 3,4,5-TNT (δ, 27), with three contiguous nitro groups but with the methyl group having no adjacent nitro group, had an impact sensitivity of 107 cm. These results tend to suggest that the interaction between three contiguous nitro groups imparts the same sensitivity as does the interaction between adjacent methyl and nitro groups, but that a synergistic effect is produced when both features are present in the same molecule.
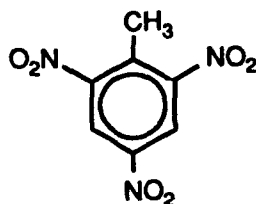
25

100 cm
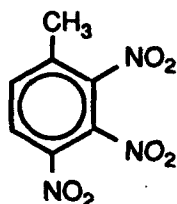
26

56 cm
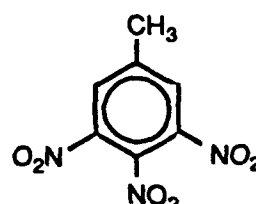
27

107 cm

Oxygen balance, OB_{100}, is clearly related to the volume and type of gaseous products other than nitrogen on explosion (either detonation or deflagration) of an energetic material and to the energy released. Therefore, it is probably more directly relevant to the propagation of reaction than to its initiation. The latter is more closely related to the strength of the critical bond and the energy required for its rupture. (This bond need not necessarily be the first bond broken, but probably usually is.) Thus the approaches of Nielsen (Reference 2), Stals (Reference 19), and Delpuech and Cherville (Reference 20) are probably more valid scientifically, but they are more complex and require data not readily available for a new or proposed explosive, and they are consequently less usable as predictive tools. The observed and undeniable correlation between oxygen balance and impact sensitivity, which is heightened by restricting the explosives to a very closely related series of compounds, is probably more coincidental than causal. Thus, in such a set of compounds the features which increase oxygen balance probably also decrease the energy required to break the critical bond to initiate reaction. However, these parallel effects may be expected to diverge as

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dissimilar features are incorporated into the molecule, and particularly so when new trigger linkages are introduced.

Experience and intuition tell us that a number of features contribute to the sensitivity and instability of explosives in general, and polynitroaromatics in particular. In the polynitroaromatics, the initial reaction is believed to involve cleavage of the $C-NO_2$ bond; an increase in the number of nitro groups leads to an increase in the number of potential initiation sites, while an accumulation of contiguous nitro groups leads to a weakening of the central $C-NO_2$ bond by both electronic and steric effects. The inclusion of an azido, diazonium, or nitramine group markedly increases the impact sensitivity, but this is achieved only by the presence of a new and more sensitive trigger linkage. An increase in the number of nitro groups in a molecule is reflected in an increase in oxygen balance; their accumulation in vicinal positions is not. Inclusion of an azido or diazonium group, or the replacement of a nitro group by a nitramine, also has a relatively minor effect on oxygen balance. Other features which contribute to sensitivity include low melting point (decomposition takes place more rapidly in the liquid state than in the solid) and molecular asymmetry.

Apparently, the presence of an α C-H bond, as in the methyl or methylene group, leads to increased sensitivity, and the very plausible justification of Kamlet and Adolph (Reference 15) has already been discussed. However, this conclusion is only valid if compounds with the same oxygen balance are considered. There is no evidence in this work that the addition of a methyl group to trinitrobenzene, tetranitrobenzene, pentanitrobenzene, or tetranitroaniline results in any large increase in impact sensitivity. The methyl group appears to act essentially as an inert diluent which happens to decrease the oxygen balance of the compound, and therefore, gives the appearance of a sensitizer if oxygen balance is considered as the other variable. Support for this hypothesis may be derived from the impact sensitivities of trinitroxylene and -mesitylene (40, 41), which are indistinguishable from that of TNT (25).
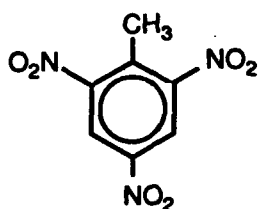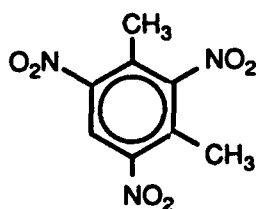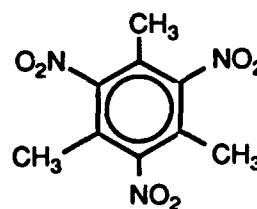
25	40	41
100 cm	100 cm	110 cm

Physical features which appear to contribute to insensitivity and stability include high molecular weight and melting point and a high degree of symmetry. The outstanding chemical feature which leads to insensitivity in polynitroaromatics is the presence of amino groups between the nitro groups around the aromatic ring. (The presence of an amino group will, of course, result in a decrease in oxygen balance.) This effect is observed most dramatically as amino groups are added sequentially in the series trinitrobenzene/picramide/DATB/TATB (4, 8, 9, 10), with the remarkable increase in stability and insensitivity, and has been attributed to strengthening and stabilizing

the C-NO$_2$ by the electron donating amines, and to intra- and intermolecular hydrogen bonding.

4	8	9	1 0
71 cm	141 cm	>200 cm	>200 cm
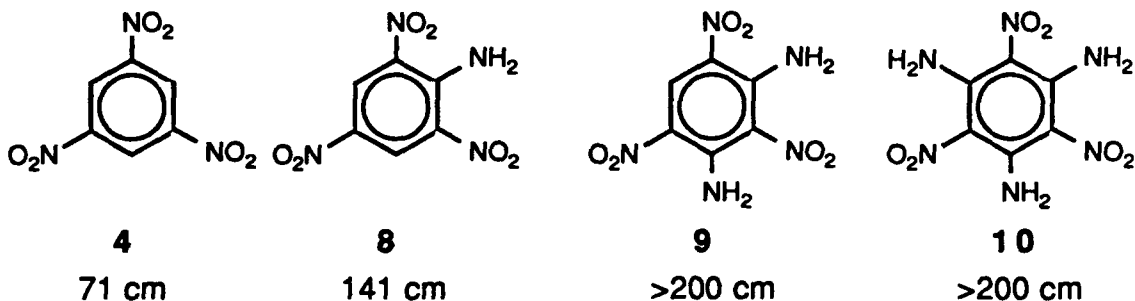
A similar effect was observed by Iyer for the series trinitrotoluene/ aminotrinitrotoluene/diaminotrinitrotoluene (25, 42, 43) (Reference 24), and can be seen in all the polynitroanilines examined in this report.

2 5	4 2	4 3
61 cm	174 cm	239 cm (Reference 24)
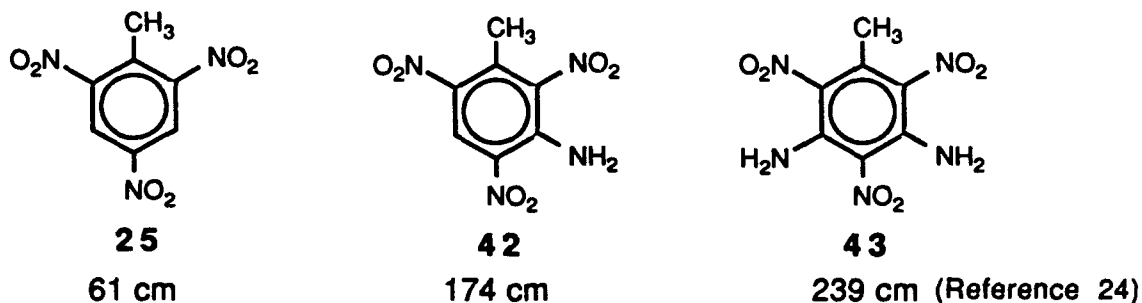
A corresponding decrease in sensitivity is also to be seen on inclusion of amino groups in benzofuroxans, going from DNBF to ADNBF to CL-14 (15, 16, 17).

1 5	1 6	1 7
76 cm	100 cm	120 cm
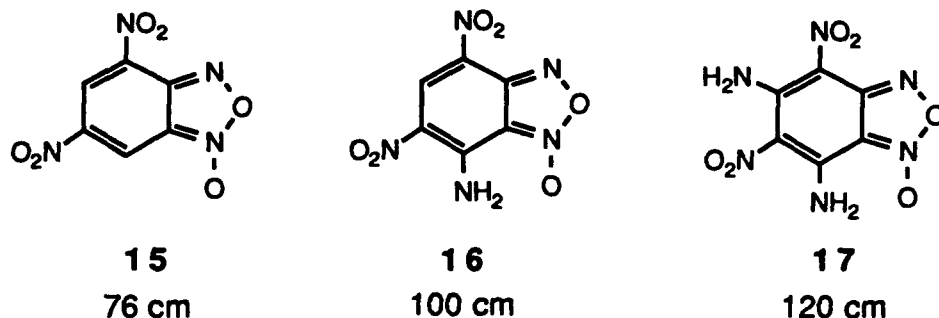
However, the effect is not universal. Read found that the impact sensitivity of hexanitrobiphenyl was actually increased by the presence of amines (Reference 25). This result may be due to steric factors, with the orthogonality of the biphenyl ring system and steric crowding of the substituents forcing one of the ortho nitro groups into an unfavorable configuation and weakening the C-NO$_2$ bond, and has prompted Read to consider benzo[c]cinnoline oxides such as 45, in which the rings are constrained in a

planar configuration, as alternatives to the orthogonal biphenyls (e.g., **44**) (Reference **26**).

44

45
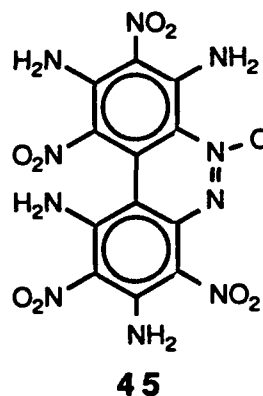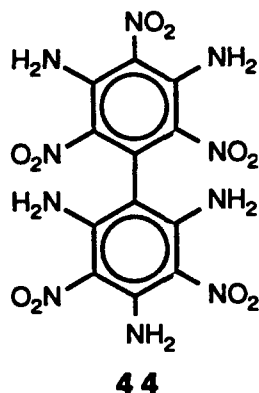
Hutchinson found that the addition of amine groups to tetryl (**37**) to give **46** also caused an increase in sensitivity (Reference **27**). However it must be recalled that in tetryl it is the N-NO$_2$ bond rather than a C-NO$_2$ bond which provides the initial reaction, and it is not unreasonable that a substituent which strengthens the latter bond might weaken the former.

37

46
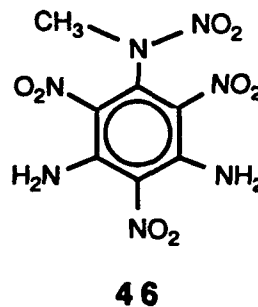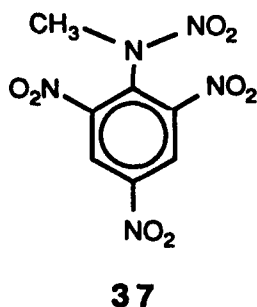
| Figure of Insensitivity (F of I) | 100 | 75 | (Reference 27) |

It seems likely, then, that the apparent correlation between the oxygen balance of an energetic material and its sensitivity to impact is an indirect and rather fortuitous one, both factors being related to the number of various sensitizing and desensitizing features. Within a closely related series in which the mode of chemical reaction and "trigger linkage" remain constant, and in which change is restricted to only the number of nitro or amino groups, a good correlation might be expected. In a more diverse collection of compounds the correlations may not be so good; when new trigger linkages are introduced any correlation would be considered surprising.

In this context, it seems worth while commenting on the impact sensitivity of some picryl and nitro substituted heterocycles synthesized recently in these laboratories. In the light of the discussion above, polynitroheterocycles are recognized as distinctly different from the polynitroaromatics already considered. However, 1-picryl-4,6-dinitrobenzimidazole (**47**), with an oxygen balance of -2.63 and an

impact sensitivity of 91 cm, lies surprisingly close to the trend for the polynitro-aromatics in Figure 2. It is believed that the trigger linkage is a C-NO$_2$ bond, probably one of those in the picryl moiety. On the other hand, the corresponding 1-picryl-4,6-dinitrobenzotriazole (48) and its 5,7-dinitro isomer (49, BTX), with an oxygen balance of -1.90 and impact sensitivities of 35 and 40 cm, are much more sensitive than indicated by the trend. (Interestingly, 1-picrylbenzotriazole (50) has an even lower oxygen balance and a higher sensitivity.) In these compounds, it is believed that the initial reaction on impact involves cleavage of nitrogen from the triazole segment rather than scission of a C-NO$_2$ bond (Reference 28). It is worth noting that picryl-polynitroimidazoles and 1,2,4-triazoles also tend to be somewhat more sensitive than might be predicted from the trend in Figure 2, although not as sensitive as the benzo-triazoles since they do not contain the N=N-N atomic grouping.[*] Perhaps this suggests that the initial reaction on impact is cleavage of a nitro group from the heterocycle rather than from the picryl moiety in these compounds.
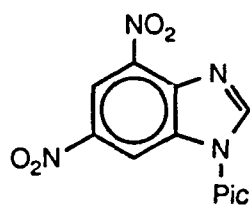
47
91 cm
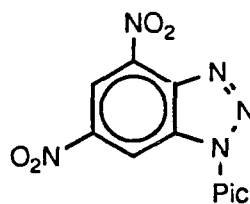
48
35 cm

49
40 cm

50
11 cm

Pic =
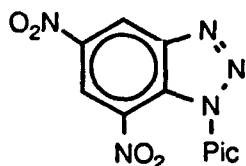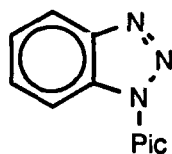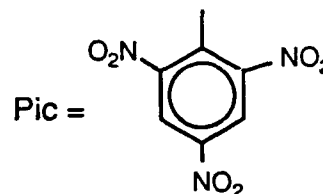
CONCLUSIONS

The velocities of detonation of polynitroaromatics studied in this report vary from about 5700 m/s for the isomeric dinitrotoluenes to over 9000 m/s for hexa-nitrobenzene and pentanitroazidobenzene (CL-16). The detonation pressures range from 166 to 403 kbar.

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[*] Unpublished results of W. S. Wilson.

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The densities of the polynitroaromatic compounds cover the range 1.65 g/cm^3 for trinitrotoluene to nearly 2.00 g/cm^3 for hexanitrobenzene. The experimental values generally correspond well with those predicted by the Holden group additivity method, with a greatest deviation of about 6%. This method overestimates the density of toluenes, benzofuroxans, and biphenyls, and underestimates the densities of molecules with alternating nitro and amino groups.

The impact sensitivity of polynitroaromatic materials ranges from about 8 to over 230 cm, with a general tendency to greater sensitivity (smaller drop height) with increasing oxygen balance. When the class of materials is tightly restricted to those containing only nitro, amino, and furoxan functional groupings, the correlation between impact sensitivity and oxygen balance is excellent. However, when other functional groups such as azido, diazonium, methyl, and methylnitramino are included, this correlation is not so good, and it appears that the relation between impact sensitivity and oxygen balance is coincidental rather than causal. Indeed impact sensitivity is more likely to be dependent on the energy of the weakest bond (the "trigger linkage"), but identification of the weakest bond and estimation of its strength are not yet amenable to simple calculation. Features which add to the sensitivity of a polynitroaromatic include the number and proximity of nitro groups, furoxan rings, azido, diazonium, and methylnitramino groups. Amino groups act as desensitizers, particularly when interspersed between the nitro groups. An additional decomposition pathway is provided by the presence of an α-methyl group, but additional methyl groups appear to have no further effect on impact sensitivity.

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Appendix

STRUCTURES OF POLYNITROAROMATIC COMPOUNDS STUDIED

HNB
1

PNB
2

TetNB
3

TNB
4

Picric acid
5

PNA
6

TetNA
7

TNA
8

DATB
9
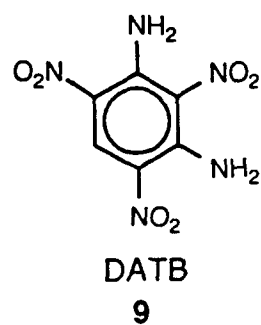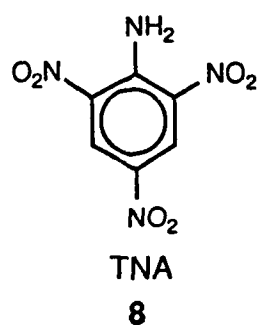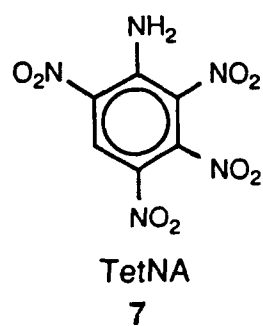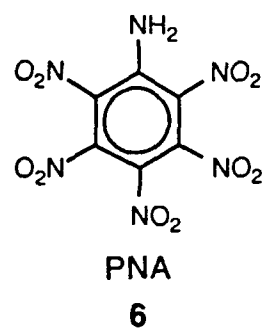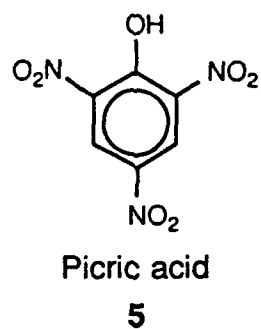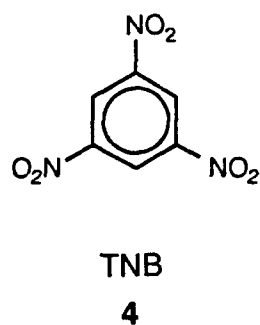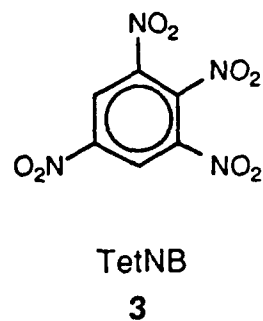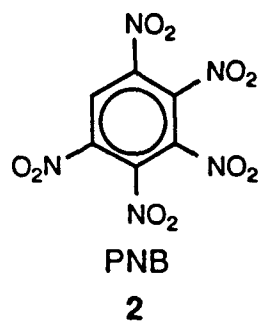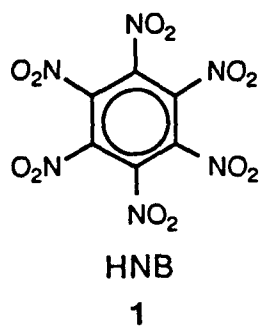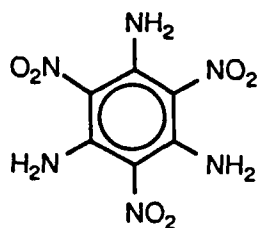
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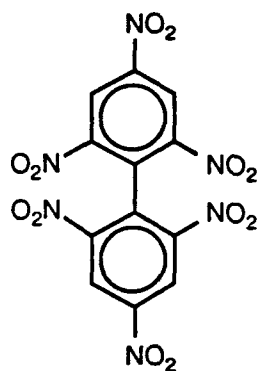
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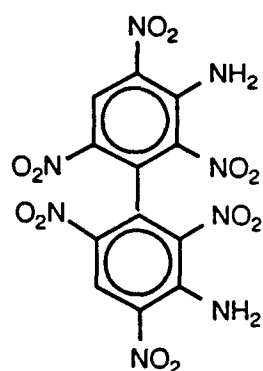
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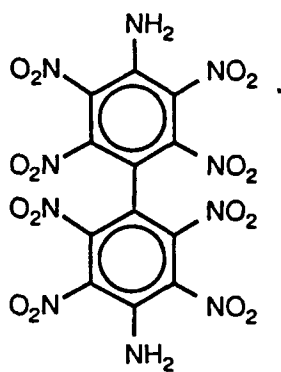
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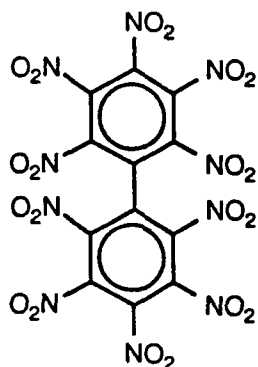
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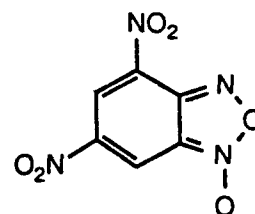
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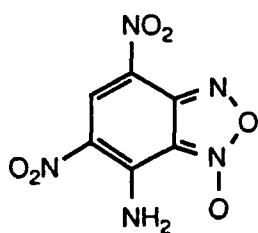
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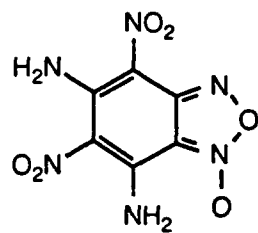
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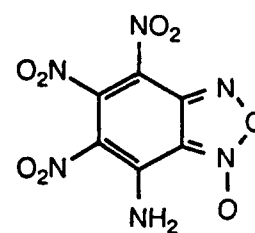
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CL-18

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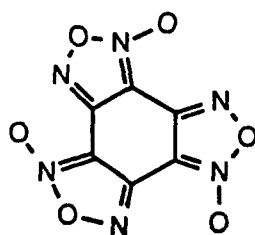
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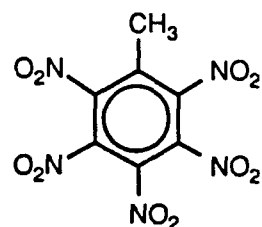
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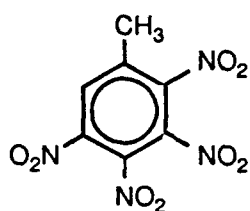
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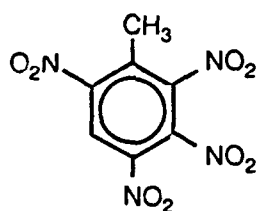
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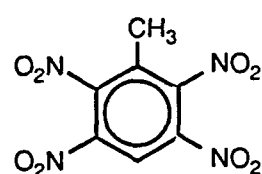
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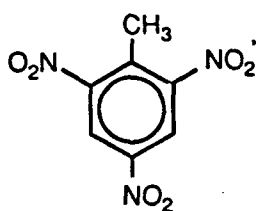
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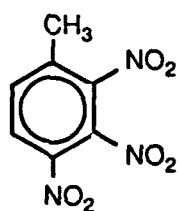
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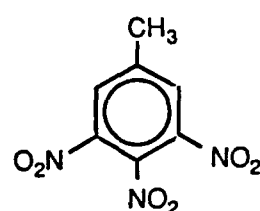
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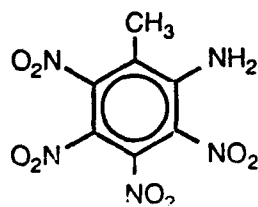
TetN-*o*-Tol

28

TetN-*m*-Tol

29

TetN-*p*-Tol

30

HNDPM
31

Picryl Azide
32

CL-16
33

DNP
34

5-Cl-DNP
35

Me-NO$_2$-DNP
36

Tetryl
37

(MeNO$_2$N)-22
38

(MeNO$_2$N)-23
39
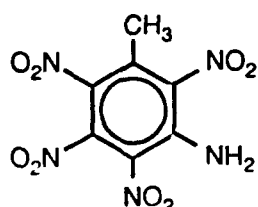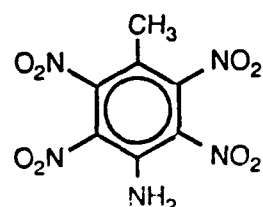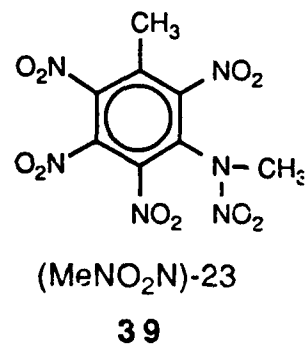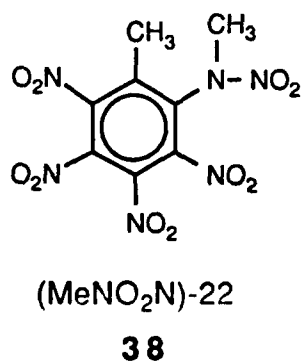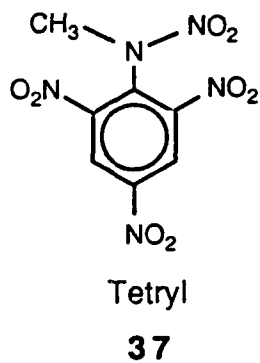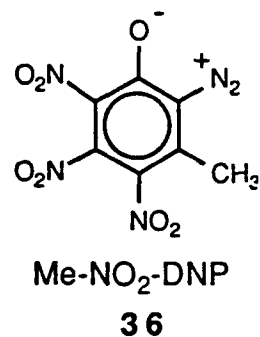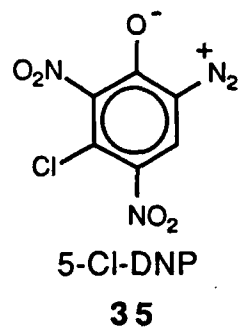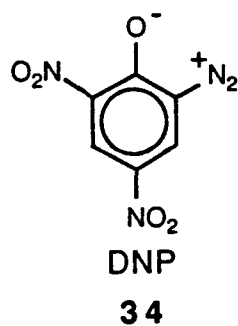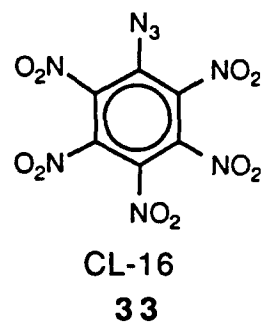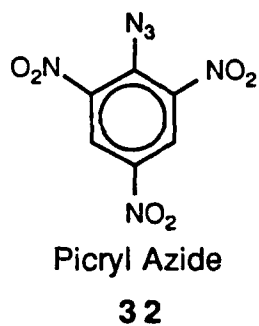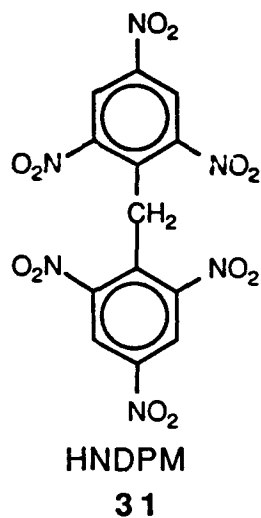
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